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Title: Methylisothiocyanate as a Wood Fumigant: Fungitoxicity to Poria carbonica in Wood and Gelatin Encapsulation for use in Wood Products

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Experiments were conducted to determine both the influence of wood moisture content on the fungitoxicity of methylisothiocyanate (MIT) to the wood-decay fungus Poria carbonica, and the ability of gelatin to safely encapsulate MIT for efficient treatment of wood products.

The fungitoxicity of MIT was studied by determining the product of fumigant concentrations and exposure times necessary to kill 90% (CT_{90} products) of the P. carbonica propagules in small Douglas-fir heartwood blocks. A continuous flow fumigation apparatus was developed that maintained constant fumigant concentrations in the air surrounding infested wood blocks. The effectiveness of MIT was determined by comparing estimates of the P. carbonica populations in the wood blocks before and after each fumigation treatment.

The CT_{90} products ranged from 46 to 179 $\mu g \cdot hr/ml$ air and were

influenced by both wood moisture content (MC) and the duration of fumigant exposure. Fungi in wood at 20% MC required about twofold higher CT_{90} products than fungi in wood at 40 or 75% MC, even though the 20% MC wood bound higher MIT concentrations. The increased fungal susceptibility in high moisture content wood should be beneficial as decay fungi are most active in wet wood. As fumigant exposures increased from 6 to 32 hr, CT_{90} products decreased about twofold, indicating a greater fungal susceptibility to MIT during long exposures and low concentrations than during short exposures and high concentrations. This suggests that low residual MIT concentrations may effectively prevent re-infestation of treated products.

High concentrations of MIT bound to wood blocks during fumigations, but were rapidly lost during aeration indicating that MIT is loosely bound to the wood structure. The MIT bound to wood should extend the duration of residual fumigant vapor in treated wood.

Gelatin encapsulation of MIT offers a safe and efficient method of storage, handling, and application of MIT for wood fumigation. Gelatin capsules did not significantly bind MIT or alter its fungitoxicity during storage, were impermeable to MIT vapors for over 1 year during dry storage, and readily released MIT when placed in moist wood.

Gelatin encapsulated MIT was equally effective as non-encapsulated MIT in fumigations of small Douglas-fir heartwood blocks infested with P. carbonica. In wood pole sections, the addition of only a small quantity

of water per treatment hole was sufficient for excellent release of MIT from gelatin capsules, and allowed rapid fumigant movement through the pole sections. The addition of larger quantities of water appeared to slightly reduce fumigant movement. Both encapsulated and non-encapsulated MIT treatments produced substantially higher levels of MIT vapors moving through poles than was produced by the breakdown of Vapam in wood. This was the result of both the more concentrated form of MIT and the poor conversion of Vapam to MIT in wood. Gelatin encapsulation of MIT offers a safe method of applying a concentrated and effective fumigant to wood products for control of decay fungi.

Methylisothiocyanate as a Wood Fumigant: Fungitoxicity to Poria carbonica in Wood and Gelatin Encapsulation for use in Wood Products

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Typed by Andrew Zahora

DEDICATED TO

My Parents

Elizabeth M. Zahora

and

L. Joseph Zahora

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INTRODUCTION

Large wood products, such as utility poles, often become infested with decay fungi after they have been placed in service. Infestation generally occurs after physical damage or checks penetrate the treated shell exposing untreated wood to fungal colonization. Decay fungi alter the structural properties of infested wood, reducing the product's expected service life and often necessitating costly early replacement. Volatile fungicides have proven effective in controlling internal decay of poles (Hand et al., 1970) and thus extending their service life. Currently, three agricultural fumigants (chloropicrin, Vapam, and Vorlex) are registered by the Environmental Protection Agency for use in utility poles, and the Bonneville Power Administration has estimated annual investment savings of $2.25 million by use of Vapam alone in their poles (Anonymous, 1980).

Unfortunately, the use of these fumigants is limited in many situations by application hazards. These fumigants are liquids that are applied by pouring them into holes drilled into the wood products, and then sealing the holes with wood plugs. The potential for spillage and contamination of the applicators during treatment with these liquids has limited their use for many above-ground treatments which would involve climbing the structures to apply the fumigant. The necessity for applicators to wear gas masks

when applying chloropicrin has severely limited its use due to possible public relations problems arising from applicators working in public wearing gas masks.

Methylisothiocyanate (MIT) is a promising fumigant for control of wood decay (Graham and Corden, 1980) and is a volatile solid which offers new opportunities for safer treatments under more diverse situations than are presently possible with liquid fumigants. MIT is both a highly fungitoxic component in Vorlex, and an important fungitoxic breakdown product of Vapam (32.7% solution of sodium N-methyl dithiocarbamate) in soils (Munnecke et al., 1962; and Turner and Corden, 1963), but MIT only comprises 20% of Vorlex and its yield from Vapam is considerably lower than can be attained by equal volume treatments with pure MIT. The higher fungitoxicity of MIT in comparison to Vapam is an important consideration for maximum decay control in wood products serving a structural function where drilling of treatment holes must be limited to prevent reduction in wood strength properties. At present, there is a lack of knowledge about the fungitoxicity of MIT and the influence of environmental factors on its effectiveness in wood. In addition, although MIT has reduced potential for spillage, an effective, practical method for applying it to wood products is still needed.

A major objective of this research was to develop accurate, quantitative data on the fungitoxicity of MIT by establishing the concentrations and times necessary to kill 90% of the propagules of the wood decay fungus

Poria carbonica Overh. established in small Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) heartwood blocks, and to determine if wood moisture content significantly influences the fungitoxicity of MIT. In addition, research was conducted to determine the effectiveness of gelatin encapsulation of MIT for safe and efficient handling, and subsequent release of the fumigant when the capsules were placed in wood.

LITERATURE REVIEW

The effectiveness of volatile chemicals for controlling soil pests has been known since the late 1800's, and many studies have been conducted on diffusion rates, influence of environmental factors, and relative toxicities of various soil fumigants (Goring, 1962). Similarly, time, temperature, and dosage relationships for the fumigation of grain to control such pests as the confused flower beetle have also been studied (Kenaga, 1961). Recently, a number of these fumigants have been studied for use in controlling decay fungi in wood. In 1959, Stabnikov reported that exposures of 30 g chloropicrin/cu. meter for 30 minutes effectively killed Coniophora cerebella in wood flooring. A few years later, Partridge (1961) also evaluated fumigants for control of the oak wilt fungus, Ceratocystis fagacearum, in oak logs for export. Partridge tested a number of volatile fungicides for penetration into small oak blocks and found that methyl bromide and chloropicrin effectively killed the oak wilt fungus. Methyl bromide was later demonstrated to effectively penetrate and control the oak wilt fungus in logs up to 2 foot in diameter (Jones, 1963) and recently Schmidt et al. (1982) further confirmed the feasibility of using methyl bromide to eradicate the oak wilt fungus from both black and white oak logs.

In 1962, O. F. Hand and A. F. Wetsch of the Bonneville Power Administration began studying the use of volatile fungicides for controlling decay fungi and insects in wood utility poles (Belsher, 1968). Ricard et al.

(1968) investigated the penetration of methyl bromide into Douglas-fir poles for control of incipient decay, and the use of ammonia and methyl bromide to form fixed ammonium bromide salts inside the wood for residual fungitoxicity. Hand et al. (1970) successfully controlled internal decay in Douglas-fir transmission poles by pouring the agricultural fumigant Vapam into holes drilled into the poles, and then sealing the holes with treated plugs. The effectiveness of fumigant treatments has been further developed in Douglas-fir poles by Graham and Corden (1980), in laminated timbers by Goodell (1979), and in southern pine poles by Zabel et al. (1982). The use of some of these fumigants has also recently been studied for control of Phellinus weirii, the laminated root rot, in Douglas-fir stumps (Thies and Nelson, 1982).

Concept of Dose

Dosage-response relationships in toxicological studies describe the response of organisms to a series of exposures to toxic chemicals. The resulting curves are generally sigmoid in nature when expressed on an arithmetic scale as a percentage of the maximum possible response, and are descriptive of the variation in susceptibility between individuals of a population. For comparisons, these curves can be straightened by transforming data into a probit scale of response, and a log scale of dosage. Whereas the concentration of non-volatile toxicants generally remains relatively constant after an initial application, the concentration of vapor phase toxi-

cants can change rapidly with time, and knowledge of the resulting duration of fumigant concentrations is important in determining the actual dosage. The dosage for fumigations has been defined as the cumulative product of concentration and time (CT). Theoretically, the CT product, or "dose", required for a specific toxicity should remain constant at any given temperature (Harris, 1963). Goring (1967) pointed out that the CT concept is logical if the external concentration of toxicant is directly proportional to the concentration of toxicant in the organism, and that this internal concentration is inversely proportional to the time required for death. These requirements may not be satisfied under conditions of high concentrations and short exposures, where diffusion into the organism may be restricted, or low concentrations and long exposures, where detoxification may become a factor. Deviations from the expected response to a CT product have been observed in soils by Munnecke et al. (1978) who found that 10 soilborne fungi were uniformly more sensitive to methyl bromide at high concentrations and short exposures, than low concentrations for longer exposures. Goodell (1979) observed the reverse relationship in wood where Gloeophyllum saepiarium was found to be more sensitive to chloropicrin at longer exposures than at shorter exposures with the same CT product.

Environmental Influences on Fumigations

A variety of soil environmental factors can influence the effectiveness of soil fumigations (Goring, 1962; Goring, 1967; and Smelt and Liestra,

1972). Soil moisture content can influence soil fumigations in two ways: first, through changes in the rate of diffusion; and second, by influencing the organism's susceptibility to the fumigant. Although wood differs from soil as a substrate, many of the basic concepts of soil fumigations are still important in understanding the movement and toxicity of fumigants through porous substrates.

The rate of fumigant diffusion through soil is dependent on the continuity of air spaces and the distribution of the fumigant between the aqueous, vapor, and solid phases of the soil (Goring, 1962). Fumigant solubility in water is important for effective control since most soil microorganisms are surrounded by a water film which may protect them from direct action by the fumigant vapors (Munnecke and VanGundy, 1979). Sorption of fumigants by soils increases with increasing soil organic matter which often reduces a fumigant's effectiveness by reducing its availability as a toxicant (Goring, 1967).

Fumigant toxicity to soil fungi generally increases with increasing soil moisture, and fungi in dry soils usually are more resistant to fumigants than fungi in wet soil. The decreased fungal kill in dry soils is probably not only the result of increased sorption of the fumigant by the soil solids, but may also reflect inherant toxicant resistance by organisms in dry soils (Munnecke, 1972).

The influence of the moisture content (MC) of sclerotia and microsclerotia of two soil fungi on the effectiveness of fumigants depended on the

fumigant used (Munnecke et al., 1982). For example, the effectiveness of chloropicrin over a range of exposures was greatly enhanced in saturated propagules (150 % water) compared to moist propagules (45% water). Conversely, the effectiveness of methyl bromide was less sensitive to moisture content, with moist propagules being more sensitive during short exposures and saturated propagules being more sensitive during longer exposures.

Increasing soil moisture can either increase of decrease overall fumigant effectiveness depending on the relative influences on fumigant diffusion rates, sorption by soils, and toxicities to the organisms (Goring, 1962).

In wood fumigations for insect control, the use of fumigants with low wood sorption properties is beneficial since they allow quicker and better fumigant penetration and more rapid removal during subsequent aeration (Harris, 1963). The selection of a fumigant with low wood sorption properties is probably not as important for controlling decay in large wood structures. Unlike agricultural soil and grain fumigations, poles and other large wood structures need not be taken out of service for treatment and the rate of fumigant penetration is not as critical. Furthermore, the binding of fumigants to the wood can prolong retention and residual fungitoxicity. In wood poles treated with chloropicrin or Vorlex this residual fungitoxicity can last up to 10 years after treatment (Graham and Corden, 1980).

Graham and Corden (1980) also reported that chloropicrin was more effective in controlling wood-decay fungi in moist wood (36% MC) than in dry wood (14% MC) or wet wood (116% MC). In contrast, methylisothiocy-

anate was essentially equally effective at all three moisture contents tested. These experiments did not distinguish between the influence of wood moisture content on the fumigant diffusion rates, and the actual fumigant toxicity to the fungus. Graham and Corden (1980) also suggested that methylisothiocyanate (MIT) penetrated wet wood better than chloropicrin, since MIT was more effective than chloropicrin in penetrating wood below the groundline in Douglas-fir poles where moisture levels are higher. Goodell (1979) studied the rate of chloropicrin movement through Southern pine blocks held at 8%, 30%, and 60% MC and found that chloropicrin travelled faster in wood blocks at low moisture contents and had higher initial fumigant concentration peaks than in wood blocks at higher moisture contents. However, after these initial peaks, fumigant concentrations dropped more rapidly, and to a lower level in the drier blocks. Although blocks at all three moisture contents were treated with equal amounts of chloropicrin, the highest resultant doses, or areas under the CT curves, were estimated to occur between 30% and 60% MC in these experiments. The actual toxicities of these fumigant doses at the different wood moisture contents were not investigated.

Methylisothiocyanate as a Fumigant

Methylisothiocyanate remains a solid to about 36°C and readily sublimes to a fungitoxic vapor below that temperature. Although MIT has had limited direct use as a soil fumigant, it has been extensively used as a

fungitoxic component in other formulations (e.g. Vorlex, 20% MIT) and is the major volatile fungitoxic breakdown product resulting from soil applications of Vapam (Lloyd, 1962; Munnecke et al., 1962; and Turner and Corden, 1963). The breakdown of Vapam to MIT in soils is not always complete (Turner and Corden, 1963; and Smelt and Leistra, 1974) and may be influenced by soil pH. For example, the oxidative breakdown of Vapam at a pH of 9.5 produces only MIT; but an increasing quantity of a variety of other products are produced as the pH becomes more acidic, and only the release of carbonyl sulfide is detectable at a pH of 2.3 (Turner and Corden, 1963; and Goring, 1972). Graham and Corden (1980) have demonstrated that wood accelerates Vapam breakdown and the release of a volatile toxicant which is probably MIT, although the efficiency of this breakdown to MIT in wood, which is acidic in pH, was not determined.

The water solubility of MIT is relatively high (7.6 mg/ml) compared to many other fumigants (Goring, 1967). Consequently, a high proportion of the MIT will concentrate in the water phase of the substrate being fumigated (Smelt and Leistra, 1974). Water solubility is an important property for penetration into wet areas of wood, especially below the ground-line of poles where decay fungi may be active. Although MIT binding and residual toxicity in wood has not been studied in detail, residual effectiveness of up to 10 years has been reported for Vorlex, and for a shorter effective period for Vapam (Graham and Corden, 1980).

Initial studies on the toxicity of MIT to the decay fungus Poria carbon-

ica, the most commonly isolated basidiomycete from Douglas-fir poles in the Northwest (Eslyn, 1970), have been conducted in an experimental system in which complete kill of the fungus in wood blocks was determined at a site remote from where fumigant treatments were made (Graham and Corden, 1980). The actual quantity of fumigant that P. carbonica was exposed to at these sampling sites, the population of fungus in the treated wood, and the influence of the rate of diffusion on these results were not specifically monitered.

The fungitoxicity of MIT to Fusarium oxysporum spores was influenced by sulfur and carbohydrate nutrition of the fungus in studies by Cobb (1973). This suggests that all studies of MIT fungitoxicity should be conducted in substrates nutritionally similar to that in which control is desired.

Wood Fumigation Treatment Methods

Initial studies using fumigants for control of fungi such as the oak wilt fungus in wood involved placing logs to be treated in sealed chambers and introducing the fumigants into the chambers for fumigant penetration into the logs (Partridge, 1961; and Jones, 1963). External applications of fumigants were also used by Ricard et al. (1968) for controlling wood-decay fungi in Douglas-fir poles in service. Fumigation chambers were formed around the base of poles using Mylar sheeting, and methyl bromide was added to the chambers and allowed to penetrate through the surface of

the poles and into the wood.

Hand et al. (1970), treated poles internally by drilling 9/16 inch downward sloping holes into the poles, and pouring Vapam into the holes which were then sealed with treated wooden plugs. The treated areas were wrapped with vapor barrier paper in an attempt to retard fumigant loss from the poles. Graham (1973) later found chloropicrin and Vorlex to be more effective than Vapam for controlling decay fungi in Douglas-fir transmission poles and determined that wrapping the treated poles with vapor barrier paper did not significantly improve effectiveness. Cooper et al. (1974) increased the duration of chloropicrin in wood by either dissolving paradichlorobenzene in the chloropicrin or placing the fumigant in "slow-release" polyethylene vials which retarded the release of fumigant vapors in the wood.

Vapam, chloropicrin, and Vorlex are currently registered for use in wood poles, but these fumigants are difficult to apply safely in many situations. A special closed system applicator is required to safely distribute Vorlex into treatment holes. This apparatus may be cumbersome for remote structures or above-ground applications where climbing is required. Similarly the safe application of chloropicrin and Vapam as liquids may be difficult in above ground-line treatments. This is especially true for chloropicrin where applicators must wear gas masks.

Encapsulation of fumigants could simplify their application and avoid many of the handling hazards of using liquid fumigants in the field. Although

a patent (Wallace, 1951) was awarded for the use of gelatin capsules to contain fumigants for soil applications, and methyl bromide has been impregnated into silica gel powder and encapsulated into gelatin for soil fumigation of a Japanese cedar nursery (Dokai, 1981), there are no reports of fumigant encapsulation for use in wood.

GENERAL MATERIALS AND METHODS

Influence of Wood Moisture Content on Methylisothiocyanate Toxicity to Poria carbonica in Wood

Preparation of Wood for Fumigation

Small wood blocks 2.5 cm square by 0.5 cm grain length were cut from a single board of coastal Douglas-fir heartwood. Groups of 30 blocks were numbered, oven dried for 18 to 24 hr at 105-110°C, cooled, and individually weighed to the nearest 0.001g to obtain the initial oven dry (OD) weight. The blocks were then saturated by submerging in distilled water for at least 20 minutes under vacuum. Blocks were not considered saturated until they sank upon vacuum removal. The saturated blocks were placed on racks in a covered container, autoclaved (18 psi) for 30 minutes, cooled, and aerated in a laminar flow hood until their individual weights were 0.05g less than the 80% moisture content (MC) weights as determined from their original OD weights.

The blocks were inoculated by evenly distributing 50 µl of an aqueous suspension of fragmented Poria carbonica mycelium over one end grain surface of each block. This brought the blocks to their 80% MC weights. All fungal inoculations were made with an isolate of P. carbonica which had been recently isolated from inoculated wood to assure the fungus's vigor as a wood decayer. Since initial studies showed as much variation in decay

rates between blocks inoculated from the same suspension of P. carbonica as between groups inoculated with different suspensions, inoculum concentrations were not standardized between experiments.

Following inoculation, the blocks were placed in groups of three on bent glass rods in petri plates. A piece of wet filter paper covered the bottom of each plate to serve as a moisture reservoir and to aid in detecting contamination. The plates were sealed with two layers of parafilm to minimize moisture loss and contamination, and incubated at 30°C for 8 to 10 weeks. After incubation, each block was lightly scraped with a sterile razor blade to remove external mycelium and reweighed to determine moisture content. All moisture contents, unless otherwise noted, were based on the blocks original OD weights. Blocks with drastic moisture content changes (above 95% MC or below 50% MC) or with visible contamination were discarded.

The remaining blocks were divided into three groups and adjusted to either 75% MC, 40% MC, or 20% MC. The moisture contents were adjusted downward in two steps over a time period of at least 2 weeks. First, 1/3 of the blocks in each group were adjusted to 78% MC and 2/3 of the blocks were adjusted to 43% MC by aerating them in a laminar flow hood. The blocks were then resealed in petri plates and incubated at 20-23°C for an additional 1 to 2 weeks. Then the blocks were rescraped and their moisture contents were adjusted to form three groups of blocks; one at 75% MC, one at 40% MC, and the last group at 20% MC. These blocks were

incubated for at least 1 additional week at 20-23°C to equilibrate the fungus at each moisture content prior to use in fumigation experiments.

Ten blocks which were not required for fumigation experiments were removed from four different block decay groups and oven dried to determine block weight losses. These blocks, decayed by the above procedures, had a mean weight loss of 4.8% (± 1.9%), including an average of 0.3% weight loss that occurred during the preparation of the wood blocks for inoculation.

Prefumigation Fungal Population Estimates

The toxicity of MIT to individual P. carbonica propagules in wood could not be directly determined because viable propagules within the wood could only be identified by destructive sampling. Instead, fumigant toxicity was determined by comparing estimates of the fungal population in each block before and after fumigation.

Before fumigation, the blocks were thoroughly scraped with a razor blade to remove external fungal mycelium and weighed. Blocks which had less than 16%, 34%, or 65% MC in the 20% , 40%, and 75% MC classes, respectively, were not used. A 0.5 by 2.5 cm radial face from each block was trimmed to 0.5 by 1.5 cm, and about 2 mm of the old radial face was removed. From this new face, either eight 60 µm thick sections from the 20% MC blocks, six 60 µm thick sections from the 40% MC blocks, or four 60 µm thick sections from the 75% MC blocks were cut using a sliding

microtome and saved for testing. Between every two sections that were saved, a similar section was discarded. The saved sections were then moistened with sterile distilled water to reduce fungal desiccation prior to being used to estimate fungal population levels in the blocks.

The wood sections were homogenized in 10 ml of sterile distilled water with a Servall Omni-mixer at about 11,000 rpm for 60-80 seconds. The contents were then shaken and rehomogenized for 50-60 seconds. All homogenization was done in an ice bath to prevent heating of the wood samples. The ground wood suspensions were then warmed in a water bath to about 30°C and mixed with 65 ml of potato-dextrose-agar (PDA) at 43°C. The final wood-medium suspension, containing 2 ppm benomyl and 1% agar, was adjusted to pH 4.5 with lactic acid and distributed equally between five petri plates.

Fumigant Treatment

Wood blocks were fumigated in a continuous flow apparatus similar in principle to that described by Kolbezen and Abu-El-Haj (1972) and used by Munnecke et al. (1978) for soil fumigations. The apparatus (Fig. 1) uses a split flow of water-purified compressed air, part of which becomes saturated with MIT vapors while passing through a condensor lined with purified MIT and maintained at 20.5°C. By varying the relative size of the restrictors used to split the original air flow, the MIT saturated air can be diluted to obtain a range of MIT concentrations. All restrictors consisted

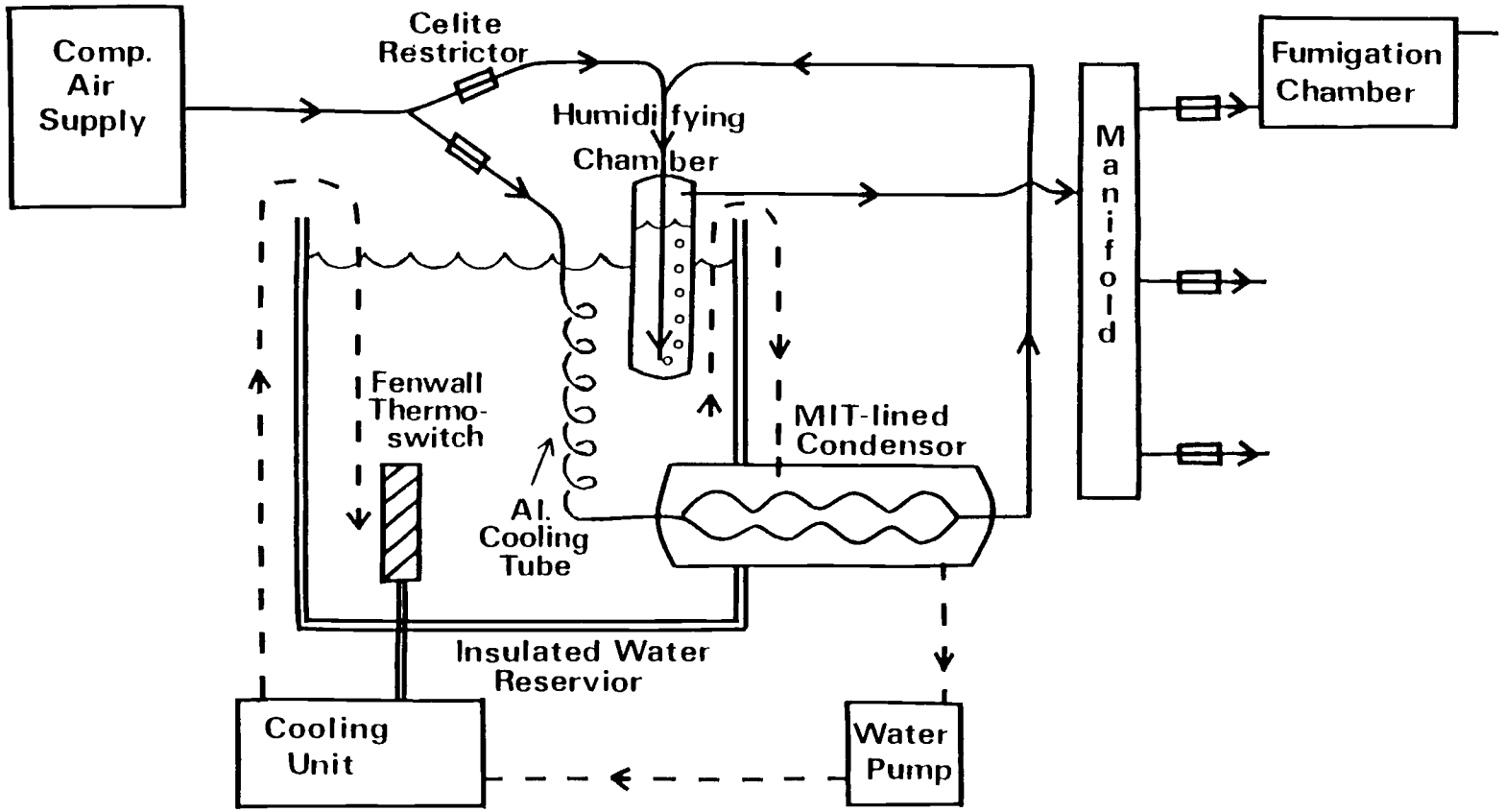

Fig. 1. Apparatus used to maintain constant methylisothiocyanate (MIT) vapor concentrations surrounding infested Douglas-fir heartwood blocks. Solid lines indicate the direction of air flow through the apparatus, while dashed-lines indicate the direction of water flow in the apparatus. Water temperature was 20.5°C (±0.25°C) to maintain a constant temperature surrounding portions of the apparatus where MIT vapor was in equilibrium with either solid MIT, or MIT in water.

of pyrex tubes packed with diatomaceous earth (Celite) held in place with packed glass wool plugs.

After the two air flows were mixed, the fumigant mixture was humidified by bubbling it through water held at 20.5°C. This minimized moisture loss from infested wood blocks during fumigation and, after an equilibrium was established between MIT in the water and gas phases, also helped buffer fluctuations in the MIT vapor concentration entering the fumigation chambers. The flow rates were maintained at 20 ml/min/chamber by the Celite packed restrictors and did not require adjustments during fumigations. This flow rate completely flushed the 300 ml fumigation chambers every 15 minutes. The entire apparatus was run for at least 12 hr to equilibrate prior to introducing the blocks for fumigation. Usually three chambers were fumigated in parallel, with each chamber containing four infested blocks at one of the three wood moisture content levels tested.

MIT concentrations in the fumigant mixture were periodically monitered throughout the experiments. Air samples were obtained with a gas tight syringe through a septum located just before the point where the fumigant mixture entered the fumigation chambers. The air samples were analyzed for MIT content by gas-liquid chromatography (GLC) procedures described below. MIT vapor concentrations entering the fumigation chambers were averaged to determine the mean concentration during each fumigation. The minor fluctuations observed in fumigant concentrations (usually less than $\pm$ 7% of mean) were considered to be insignificant and partially

due to sampling errors.

Fumigant toxicity studies usually maintain constant fumigant concentrations and vary exposure times. The reverse conditions were used in these experiments because with the apparatus used it was easier to maintain exposure times constant between experiments than to reproduce exact concentrations of MIT entering the fumigation chambers.

Postfumigation Wood Block Sampling

Immediately following fumigation of the wood blocks, two small pieces about 0.8 cm square by 0.5 cm grain length were quickly chipped from each block. One piece was extracted in 1 ml of chromatographic grade ethyl acetate for at least 4 hr for determination of the MIT concentration by GLC procedures. The other piece was weighed, oven dried, and reweighed to determine wood moisture content. The moisture content of each fumigated block was estimated by averaging its prefumigation moisture content (based on predecayed OD weight), and the postfumigation moisture content (based on the moisture content of the small subsample chipped from each block).

The remainder of each fumigated block was aerated for 2 hr in a 300cc chamber using a 1500-2000 ml/min air flow that had been humidified and scrubbed by bubbling through water. This aeration generally reduced the MIT concentrations in the wood to 3-8% of the pre-aerated concentration in the 20% MC blocks, 0.5-5% in the 40% MC blocks, and 13-18% in

the 75% MC blocks. The blocks were then recut by removing 180-240 µm from the previously sampled radial face and cutting an identical number of 60 µm thick sections as was sampled prior to fumigation. The wood sections were homogenized and plated as previously described to estimate the surviving P. carbonica population in each block.

All of the dilution plates were incubated at 29°C and developing P. carbonica colonies were periodically counted in each plate until new colonies no longer appeared or the plates were overgrown with fungi. Fumigant toxicity was based on the pre- and postfumigation population estimates obtained using this dilution plate technique.

Methylisothiocyanate Sampling Procedures

All MIT analyses were made using a Hewlett-Packard 5830A Gas Chromatograph with a flame ionization detector. Chromatograph operating conditions were: a 10 foot glass column (2 mm inner diameter) packed with 10% Carbowax 20M on 80/100 Supelcoport solid support; column temperature, 110°C; injection and detector temperatures, 165°C; nitrogen flow rate, 47 ml/min.

Concentrations of MIT in all air and wood samples were determined by extracting the samples with chromatographic grade ethyl acetate. Air samples containing MIT vapors were obtained by first injecting 0.5 ml of ethyl acetate into a 5.0 ml gas tight syringe (Hamilton). A 4.5 ml air sample was then drawn into the syringe and the ethyl acetate-air mixture

was shaken for at least 15 seconds and transfered into a vial for later analysis. The concentration of MIT in all ethyl acetate extractions (both vapor and wood extractions) were determined by comparing MIT peak areas from 3.0 ul injections of the unknowns with similar injections of standard solutions of MIT in ethyl acetate. This sampling method enabled quantification of MIT vapor concentrations down to 0.08 µg/ml of air.

Gelatin Encapsulation of Methylisothiocyanate for Wood Fumigation

MIT was encapsulated into standard two-piece hard gelatin capsules. Prior to filling the capsules, a small injection hole was made in the center of each capsule top and the capsules were cleaned with acetone to remove surface oils that might hinder sealing. The capsule halves were sealed together by coating the overlapping portions with a thick, hot gelatin solution (Knox Unflavored Gelatin) and sliding the halves together. After drying, the capsule joint was recoated with gelatin. Technical grade MIT (95% active ingredient) was warmed to 40-50°C, pipetted into each capsule, and allowed to cool and solidify. Capsule tops were recleaned with acetone and the injection holes were sealed with solidified gelatin disks glued into place with a hot gelatin solution. The injection holes were then recoated twice with gelatin to insure complete sealing. Extra-long gelatin capsules, prepared by sealing together two of the longer capsule bottoms with a gelatin sleeve cut from the wider capsule tops, were filled and sealed as described above.

A number of experiments were conducted to determine the ability of gelatin to effectively encapsulate MIT for use in wood fumigations. The specific methodology of these experiments will be described in the Results and Discussion section for better clarity of purpose and results for each experiment.

RESULTS AND DISCUSSION

Influence of Wood Moisture Content on Methylisothiocyanate Toxicity to Poria carbonica in Wood

Dosage-response curves were generated describing the toxicity of MIT to P. carbonica in wood blocks at three different wood moisture contents (Fig. 2). The percent survival of P. carbonica propagules in replicate fumigated blocks varied, with individual blocks of a replicate occasionally showing either 0%, or over 100% survival. Because these extreme values could not be transformed to probits for regression analysis, the survival values for individual blocks within each treatment were averaged prior to statistical analysis. The high variability between replicate blocks was partially the result of inaccuracies inherent in estimating the pre- and postfumigation fungal populations within the wood blocks. Population estimates were made by sampling equal volumes of wood from separate but adjacent portions of the infested blocks, but the distribution of the fungus within each block was not necessarily uniform.

The effectiveness of MIT was influenced by the moisture content of the wood colonized by P. carbonica (Fig. 2). Poria carbonica in wood blocks ranging from 17-22% MC showed consistently higher survival levels than in similarly infested wood blocks which ranged from 36-43%, or 66-80% MC. For convenience, the wood blocks in the three moisture content ranges, 17-22%, 36-43%, and 66-80%, will be refered to as 20%, 40%, and 75% MC

Fig. 2. Dosage-response relationships describing the influence of wood moisture content on the fungitoxicity of methylisothiocyanate (MIT) to Poria carbonica growing in Douglas-fir heartwood blocks. Infested wood blocks were at either 17-22% MC ○, 36-43% MC ●, or 66-80% MC △, and were exposed to constant concentrations of MIT vapors for 6, 12, 16, or 32 hr periods. Each data point reflects the average survival from four fumigated blocks, which was weighted during regression analysis based on the relative variance between the survival values in each treatment.

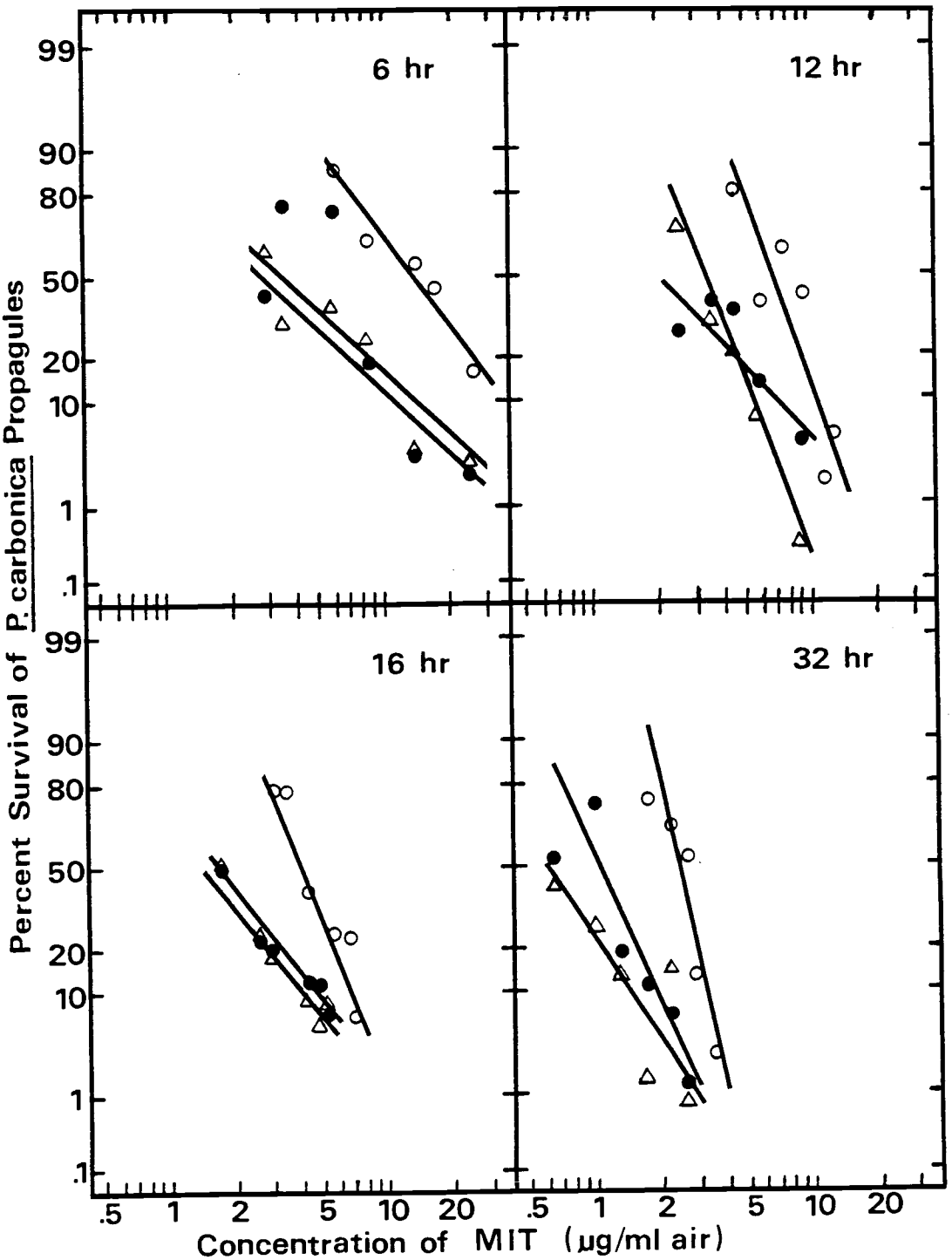

Fig. 2. Dosage-response relationships describing the influence of wood moisture content on the fungitoxicity of methylisothiocyanate (MIT) to Poria carbonica

blocks, respectively. These wood moisture contents represent the average value within each block and small areas of the blocks may be at slightly higher or lower moisture contents. A statistical comparison of the regression lines in each fumigation time period (Table 1) showed that the MIT dosage-response plots for P. carbonica in 20% MC wood were significantly different than the dosage-response plots for P. carbonica in 40% and 75% MC wood. Conversely, the dosage-response plots for P. carbonica in 40% and 75% MC wood were not statistically different after 6, 16, and 32 hr exposures. Although a statistical difference ($p < 0.05$) was observed in the 40% and 75% MC wood after 12 hr exposures, this was attributed to a trend for the error variances in these plots to be unequal (Fig. 2) and to the poor fungal survival in the 40% MC wood at low MIT concentrations. Even though the 40% and 75% MC plots were statistically different after 12 hr fumigations, the regression lines intersected and displayed similar toxicity results over the mid range of MIT concentrations tested.

The slopes of the dosage-response curves showed a tendency to become steeper with increasing fumigant exposure time at all three wood moisture contents. This suggests that there is less variability in the susceptibility of P. carbonica propagules to MIT fumigation during longer exposures. The resulting influence on MIT toxicity will be further discussed below.

The dosage-response curves were used to generate concentration-time (CT) curves describing the product of fumigant concentrations and

Table 1. Statistical comparison of dosage-response regression lines from Fig. 2

Fumigation time period	Dosage-response plot comparison (% MC)[1]	F* value	Critical F value[2]
6 hr	20, 40, and 75	13.76	F(.99;4,11)=5.67
	20 and 40	23.30	F(.99;2,7) =9.55
	20 and 75	21.18	F(.99;2,7) =9.55
	40 and 75	0.50	F(.50;2,8) =0.76
12 hr	20, 40, and 75	8.57	F(.99;4,10)=5.99
	20 and 40	5.26	F(.95;2,7) =4.74
	20 and 75	13.44	F(.99;2,7) =9.55
	40 and 75	8.92	F(.95;2,6) =5.14
16 hr	20, 40, and 75	24.55	F(.99;4,11)=5.67
	20 and 40	35.36	F(.99;2,8) =8.65
	20 and 75	33.76	F(.99;2,8) =8.65
	40 and 75	0.74	F(.50;2,8) =0.76
32 hr	20, 40, and 75	23.83	F(.99;4,11)=5.67
	20 and 40	40.77	F(.99;2,7) =9.55
	20 and 75	29.35	F(.99;2,7) =9.55
	40 and 75	1.56	F(.75;2,8) =1.66

[1] Actual moisture content (MC) ranges were: 20%=17-22%; 40%=36-42%; and 75%=66-80%.

[2] Reduced models include all data points from the regression plots being compared. Alternative conclusions are: if $F^* \leq F(1-\alpha;r-1, n_t-r-1)$, then the lines are similar in both slope and intercept, or; if $F^* > F$, then at least one line in the comparison must differ with respect to either slope and/or intercept with the other lines in the comparison.

exposure times necessary for MIT to kill 90% (CT_{90} products) of the P. carbonica propagules in wood at the three different wood moisture contents (Fig. 3). As with the dosage-response plots, the CT_{90} product plots also were influenced by the wood moisture content. A statistical comparison of the CT_{90} regression lines (Table 2) showed that P. carbonica in wood at 20% MC required significantly higher CT_{90} products than fungi in wood at 40% and 75% MC, but that there was not a statistically significant difference in CT_{90} products required to control the fungi in wood at 40% and 75% MC. Numerical values for the difference in CT_{90} products required in wood at these three moisture contents are presented in Table 3, and demonstrate that about 2 fold higher CT_{90} products are required in 20% MC wood than in 40% or 75% MC wood.

The greater resistance of P. carbonica propagules to MIT in wood blocks at 20% MC, than in the wetter blocks, is probably due to the fungus being metabolically less active in the 20% MC wood. The fiber-saturation point of Douglas-fir heartwood is about 28% MC, and wood moisture contents below this value theoretically have no free water in the wood cell lumens. Fungi in wood below the fiber-saturation point do not actively grow and decay wood because free water is not available for diffusion of extra cellular fungal enzymes and their degredation products, and because cell wall micropores shrink making the cellulose inaccessible to the enzyme molecules (Griffin, 1977). Conversely, the wood blocks at both 40% and 75% MC are above the fiber-saturation point of Douglas-fir heartwood

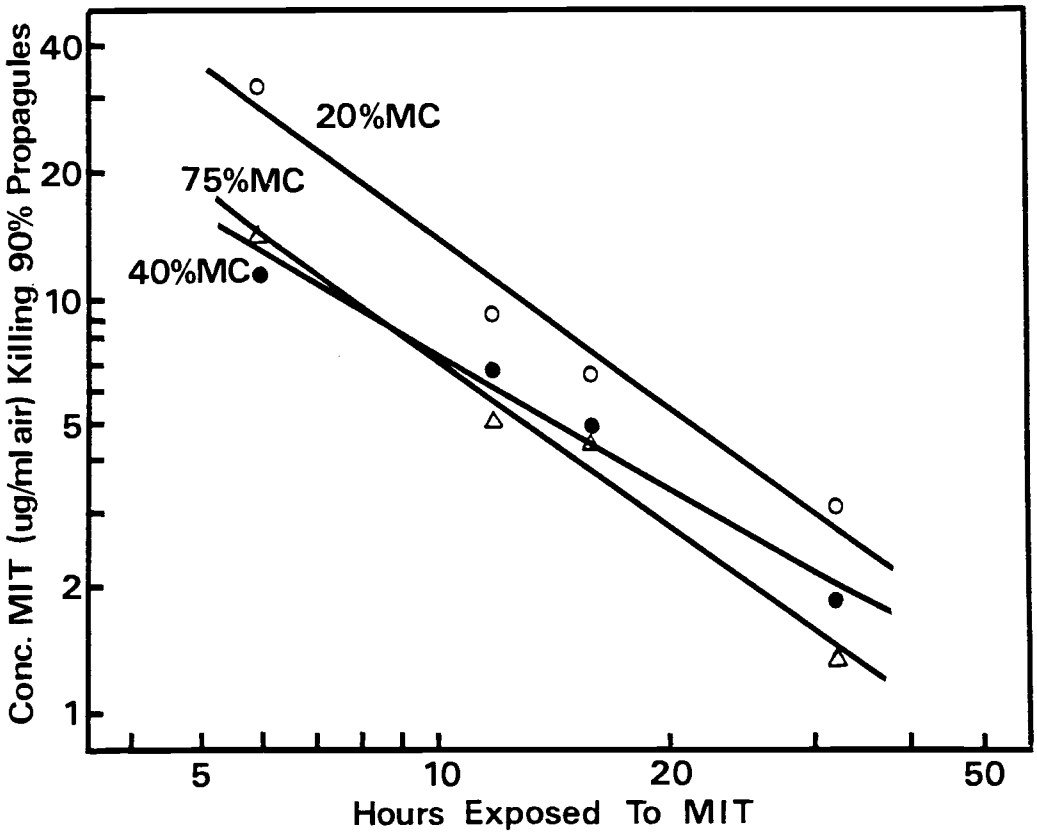

Fig. 3. Relationship between methylisothiocyanate (MIT) concentrations and exposure times required to kill 90% of the Poria carbonica propagules in Douglas-fir heartwood blocks at various wood moisture contents: ○ = 17-22% MC, ● = 36-43% MC, and △ = 66-80% MC.

Table 2. Statistical comparison of methylisothiocyanate CT_{90} [1] regression lines from Fig. 3

CT_{90} plot comparison (% MC of wood)	F* value	Critical F value[2]
20, 40, and 75	8.19	F(.975;4,6)=6.23
20 and 40	9.07	F(.95;2,4) =6.94
20 and 75	12.50	F(.975;2,4)=10.6
40 and 75	1.48	F(.75;2,4) =2.00

[1] The product of methylisothiocyanate concentrations and exposure times required to kill 90% of the Poria carbonica propagules in Douglas-fir heartwood blocks.

[2] Reduced models include all data points from the regression plots being compared. Alternative conclusions are: if $F^* \leq F(1-\alpha;r-1, n_t-r-1)$, then the lines are similar in both slope and intercept, or; if $F^* > F$, then at least one line in the comparison must differ with respect to either slope and/or intercept with the other lines in the comparison.

Table 3. Methylisothiocyanate (MIT) concentrations X times (CT products) necessary for 90% kill of the Poria carbonica propagules in Douglas-fir heartwood blocks at three different wood moisture contents

Length of exposure	CT products[1] (µg MIT/cc air X hr) for 90% kill of P. carbonica in wood at various moisture contents		
	17-22% MC	36-43% MC	66-80% MC
6 hr	185	79	90
14 hr	130	74	66
32 hr	92	68	48

[1] The CT products were obtained from the regression lines in Fig. 3.

and fungi in these blocks should be actively growing.

Theoretically, the dose, or cumulative CT product, required for a given level of control by a fumigant should be independent of the duration of exposure, providing that fumigant uptake is not limited and the concentration of fumigant in the organism is inversely proportional to the time required for death (Goring, 1967). However, a lower CT_{90} product was required with MIT fumigations of P. carbonica propagules in wood during long exposures than during short exposures at all three different wood moisture contents (Table 3). This was particularly evident in wood at 20% and 75% MC where an almost two-fold higher CT_{90} product was required during the 6 hr fumigant exposures than during the 32 hr exposures. Goodell (1979) also found that chloropicrin CT products decreased with increasing exposure times for wood wafers infested with both Gloeophyllum saepiarium and Poria sp. He found over a ten-fold decrease in CT products for G. saepiarium during 24 hr exposures as compared to 4 hr exposures, but only a slight decrease (1.1 fold) for the Poria sp.

The increased susceptibility of P. carbonica to MIT fumigations during longer exposures may be important in defining residual effectiveness of fumigants in large wood structures where low fumigant concentrations have been detected for years after the initial treatment (Graham and Corden, 1980), and in determining the rate and effective range of fumigant movement through wood. Information on the effects of longer fumigant exposure periods is needed to determine both the limit of increasing MIT toxicity

with increasing exposure time, and the minimum lethal MIT concentration to P. carbonica.

The P. carbonica infested Douglas-fir heartwood blocks used in the toxicity studies were also monitored for MIT sorption after each fumigation by measuring the MIT extractable in ethyl acetate. This included MIT bound to the wood structure, in the air, and dissolved in the water within the wood. The highest quantity of MIT was sorbed by wood at 20% MC, the least by wood at 40% MC, and an intermediate amount by wood at 75% MC throughout the range of MIT vapor concentrations and exposure times tested. these relationships between MIT vapor concentrations and MIT sorbed by the wood blocks (slopes of the lines in Fig. 4) at the three different wood moisture contents were statistically different from each other ($p<0.001$), with the 20% MC blocks sorbing almost 50% more MIT than the 40% MC blocks. An identical relationship between wood moisture content and quantity of MIT sorbed by infested wood was also observed during 6 hr and 12 hr fumigations, although these results were not included in Fig. 4.

The MIT sorbed by the fumigated blocks was principally bound in some way to the wood structure. For example, wood at 75% MC and exposed to 2 µg MIT/ml air for 32 hr sorbed a total of 1000 µg of MIT/g of OD wood (Fig. 4). Douglas-fir heartwood at 75% MC contains about 1 cc of air and 0.5 ml of free water (water above fiber-saturation point) per g of OD wood. Based on an MIT distribution ratio between water and air of 150:1 at 22°C (estimated from Smelt and Leistra, 1974), about 0.3 mg MIT should be dis-

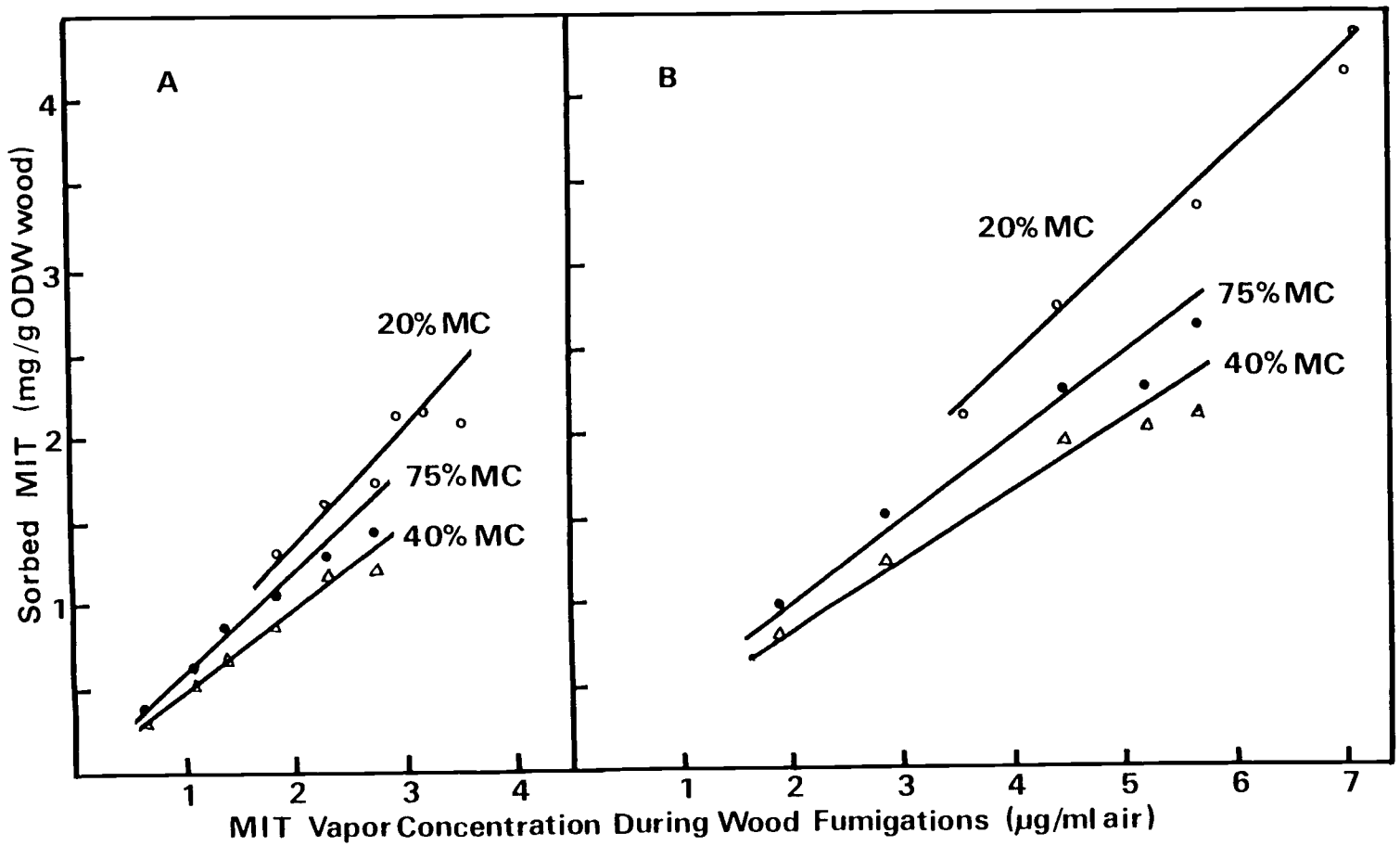

Fig. 4. Influence of wood moisture content on methylisothiocyanate (MIT) sorption by Poria carbonica infested Douglas-fir heartwood blocks following exposures for: A) 32 hr, and B) 16 hr, to air containing various concentrations of MIT vapors. Moisture contents of the infested blocks (oven-dry weight basis) ranged from 17-22% (20% MC), 36-43% (40% MC), and 66-80% (75% MC). Each point is the average sorption of four blocks fumigated together. The slopes of the sorption curves for the wood blocks at each moisture content are statistically different from each other ($P < 0.001$) within each of the two fumigation time periods.

solved per ml water at 2 µg MIT/ml of air. Therefore, of the 1000 µg MIT per g of OD wood, only about 150 µg MIT should be dissolved in the water, and about 2 µg MIT in the air within the wood, with the rest of the MIT (848 µg/g OD wood) bound in some way to the wood structure, including the fungus within the wood. The total MIT sorbed by wood blocks at 20% MC was considerably higher (Fig. 4), even though no free water should be present in this wood. This suggests that essentially all of this MIT must be bound to the wood structure.

The greater total sorption of MIT by wood at 75% MC than at 40% MC was mostly a result of MIT dissolved in the larger quantity of water. The higher observed MIT sorption by the dry wood (20% MC), in comparison to wood at the higher moisture contents, suggests that water may interfere with the ability of MIT to bind to the wood structure.

Although P. carbonica was less susceptible to MIT in the wood blocks at 20% MC, these blocks bound more fumigant at any given vapor concentration than blocks at higher moisture contents. This was the reverse of expectations since the infested wood with the highest total fumigant sorption (20% MC wood), also had the highest level of survival. This suggests that the MIT bound to the wood structure is probably less effective in controlling P. carbonica than the MIT in the air and water surrounding the fungus. Thus, the total MIT content of wood, taken without knowledge of wood moisture content, will be a poor estimator of expected control. The reduced effectiveness of MIT in dry wood may reflect a lower rate of fungal

metabolism in dry wood.

Even though MIT was less effective in controlling P. carbonica in dry wood than in wet wood, it was still highly fungitoxic over the broad range of wood moisture contents tested. The increased susceptibility of P. carbonica in wet wood to control by MIT may be beneficial during fumigations of large wood structures where fumigant penetration into wet areas of wood may be hindered. Furthermore, control of decay fungi in wet areas of the wood is desired as this is where active decay and wood degredation are most likely to occur.

The majority of the MIT that is sorbed by Douglas-fir heartwood during exposures to MIT vapors was found to be loosely bound to the wood structure and rapidly lost during aeration. Douglas-fir heartwood blocks (0.8 cm x 2.5 cm x 0.5 cm grain length) that were decayed with P. carbonica for 8 weeks at 28°C and had a wood moisture content of about 80% were used to study the retention of MIT by wood after aeration for different time periods. Blocks were exposed to an MIT saturated atmosphere (about 48 µg MIT/cc air) for 27 hr and then removed and aired in a fume hood. After specific lengths of aeration, both springwood and summerwood bands were chipped from the blocks, extracted in 1.0 ml of ethyl acetate for 4 hr, and the MIT concentrations determined by GLC methods.

Absolute MIT concentrations remaining in these small wood blocks after aeration treatments varied between replicate blocks, but MIT concentrations always decreased rapidly during aeration, especially in the spring-

wood bands where MIT was barely detectable after 2 hr (typical results in Table 4). Concentrations of MIT were initially higher in the springwood bands than in the summerwood bands (32 vs 26 mg MIT/g of OD wood), although this probably resulted from the higher moisture content of the springwood. Although the blocks averaged 80% MC prior to aeration, the springwood bands were about 110% MC, whereas the summerwood bands were only about 60% MC. This increased springwood water content can account for almost 4 mg MIT per g of OD wood as MIT has a solubility in water of 7.6 mg/cc at 20°C (Goring, 1967).

MIT was bound in springwood and summerwood bands at similar concentrations (based on OD weight of wood), even though the tracheid surface area was much higher in the springwood. This suggests that MIT may bind throughout the tracheid walls and not just to the surface of the tracheids. The slower desorption of MIT in summerwood during aeration is probably the result of the thicker cell walls from which bound MIT must diffuse, and the smaller tracheid lumens from which MIT vapor must diffuse.

While the ability of Douglas-fir heartwood to bind MIT in large quantities may reduce the rate of MIT movement through wood poles, it should increase the length of residual fumigant activity. The sorbed MIT is loosely bound to the wood structure and may act as a reservoir to maintain a sufficient level of MIT in the vapor phase to effectively control decay fungi.

Table 4. Retention of methylisothiocyanate (MIT) by Poria carbonica infested Douglas-fir heartwood blocks following aeration in a fume hood[1]

Aeration time	MIT (mg) per gram of oven dry wood	
	Springwood	Summerwood
15 sec	32	26
60 sec	24	26
5 min	11	22
15 min	3.0	18
30 min	0.98	14
60 min	0.41	6.6
2 hr	0.09[2]	1.5
8 hr	0.04[2]	0.32
24 hr	0.02[2]	0.24

[1] Blocks were 2.5 cm by 0.8 cm by 0.5 cm grain length, and were infested with P. carbonica for at least 8 weeks at about 80% MC prior to treatment.

[2] Values were estimated from strip chart recordings as the MIT peaks were too small to be automatically integrated by the gas chromatograph.

Gelatin Encapsulation of Methylisothiocyanate for Wood Fumigation

An ideal fumigant encapsulating material should be inert to the fumigant to minimize interference with the fumigant's effectiveness, be impermeable to the fumigant prior to application for safe storage and handling, and become permeable to the fumigant for release from the capsule following treatment. The following studies were conducted to determine the ability of gelatin to satisfy these requirements for use as an MIT encapsulating material.

Inertness of Gelatin to Methylisothiocyanate

The ability of gelatin to encapsulate MIT without significantly interfering with the effecteveness of the fumigant was demonstrated in two ways. In the first study, the ability of gelatin to bind and thereby reduce the availability of encapsulated MIT was studied. Small quantities of MIT (20 µl) were placed in glass stoppered flasks along with a comparatively large quantity of gelatin (200 mg), a small vial containing 1.5 ml of water serving as a vapor trap, and 0.2 g of Douglas-fir heartwood sawdust at 8.5% MC. One half of the gelatin in the flasks was kept dry, and the other half was moistened with 0.2 ml of water to allow gelatin in both states the opportunity to bind MIT. Identical flasks were prepared lacking only the gelatin. The glass stoppers were sealed in place with a silicone stopcock grease and the flasks were stored at 20-22°C for 24 hr to allow the MIT to partition between the gelatin, wood, and the vapor-trap water. The vapor-trap water was

then extracted with ethyl acetate and the MIT concentrations were determined by GLC methods. Three replicate flasks were used for each test.

The concentration of MIT in the vapor-trap water in flasks containing gelatin was only slightly lower than that in identical flasks lacking gelatin (4.4-4.5 vs 4.7-4.9 mg MIT/ml water), even though there was 10 times more gelatin than MIT. This demonstrates that an insignificant amount of MIT will bind to gelatin and become unavailable for movement into wood to control decay fungi.

In the second study, the influence of gelatin on the breakdown of MIT was studied. Technical grade MIT encapsulated in a 1.0 ml gelatin capsule for over 8 months was heated, the MIT was removed, and 25 µl was transfered and dissolved in 5.0 ml of distilled water. An identical solution was prepared from technical grade MIT stored in glass over the same time period.

A bioassay was conducted to compare the fungitoxicity of the two MIT solutions. Twelve test tubes (25 ml) each containing 1/2 of a sheet of filter paper were sterilized, plugged with serum caps, and used as fumigation chambers. Varying amounts of the aqueous solution (10-500 µl) made from encapsulated MIT were pipetted onto the filter paper in one-half of the test tubes. Water was then added to make a total of 500 µl added per tube. An identical series was made using the solution made from MIT that had been stored in glass.

A group of four randomly selected wood sections (12 mm x 7 mm x 120 µm) cut from a radial face of a P. carbonica infested Douglas-fir heart-

wood blocks were placed in each test tube. After 48 hr, the wood sections were removed and ground in 20 ml of water at 11,000 rpm for 70-80 seconds using a Sorvall Omni-mix. The wood suspensions were added to 1% potato-dextrose-agar (pH 4.3) to make a volume of 85 ml, and this was poured into glass petri plates. The plates were incubated at 30°C and the number of P. carbonica colonies surviving each treatment were counted (Table 5).

The recovery of P. carbonica propagules varied slightly between treatments, probably due to differences in initial fungal populations within wood sections. But in general these two treatments were equally effective in controlling P. carbonica, indicating that storage of MIT in gelatin capsules for over 8 months did not significantly alter the fungitoxicity of the fumigant to P. carbonica. The technical grade MIT used in these experiments was supplied by NOR-AM in 1977 and was originally reported to be 95% active ingredient, but GLC analysis prior to its use in 1982 revealed it to be only about 80-85% MIT. As MIT samples age during storage, they generally become darker in color than fresh samples and develop a liquid component, suggesting a slow breakdown of the chemical. This slow breakdown did not appear to be significantly influenced by gelatin encapsulation.

Impermeability of Dry Gelatin Capsules to Methylisothiocyanate

To evaluate gelatin capsules for MIT retention during prolonged storage under dry conditions, four capsules (2.0 x 8.7 cm) made from #11 capsules (Michigan Capsule Co.) were each filled with about 17 g of technical

Table 5. Influence of methylisothiocyanate (MIT) storage in gelatin capsules on MIT's fungitoxicity to Poria carbonica

MIT storage condition	Number of P. carbonica colonies recovered from infested Douglas-fir heartwood sections[1] exposed for 48 hr to varying quantities of MIT (mg/chamber)					
	2.6	1.5	1.0	0.51	0.15	0.05
Gelatin encapsulated[2]	0	3	26	110	121	142
Glass bottle	0	3	20	94	131	102

[1] Four wood sections (12 mm x 7 mm x 120 µm) cut from an infested Douglas-fir heartwood block were randomly selected for each treatment, fumigated, and the surviving P. carbonica propagules determined by dilution plating.

[2] MIT had been stored in a gelatin capsule for over 8 months prior to use.

grade MIT and sealed. Capsules were air dried for 2 days prior to recording initial capsule weights, and then the capsules were placed in a test-tube rack and stored in a laboratory fume hood. Periodically during a 389 day storage period, the capsules were weighed to determine changes that might indicate MIT loss.

Capsule weights fluctuated slightly throughout the storage period (Table 6), probably due to uptake or loss of moisture by the gelatin capsule material depending on the air moisture content. During the 389 days of storage, capsule weight losses averaged only 0.15% of the initial MIT content of each capsule. This demonstrated that encapsulation of MIT in gelatin capsules and storage under dry conditions can permit prolonged storage of the fumigant without serious loss of MIT.

Permeability of Moistened Gelatin Capsules to Methylisothiocyanate

To determine the conditions necessary for optimum release of MIT from gelatin capsules placed in wood, the influence of wood moisture content on release was studied. Small gelatin capsules (1.0 x 2.6 cm) containing about 1.0 g of MIT were prepared and used to treat wood blocks at different moisture contents. Douglas-fir heartwood blocks (4.0 cm square by 6.7 cm grain length) were drilled at midlength to accomodate the capsules. The blocks were oven dried, weighed, and then adjusted in groups of five to the following moisture contents; 20%, 23%, 26%, 30%, 40%, and 80% MC. Most blocks were adjusted to the desired moisture contents by infiltration

Table 6. Weight changes over time of gelatin capsules containing methyl-isothiocyanate (MIT) and stored in a laboratory fume hood

Time (days)	Weight of four MIT capsules (grams)[1]			
	1	2	3	4
0[2]	20.212	20.377	20.115	20.541
7	20.221	20.383	20.129	20.551
31	20.191	20.349	20.104	20.521
181	20.151	20.301	20.062	20.473
389	20.189	20.344	20.101	20.516

[1] Empty gelatin capsules weighed about 3.1 g.

[2] Initial capsule weights (zero time) were recorded 2 days after filling the capsules to allow them to thoroughly dry and equilibrate after sealing.

with water under vacuum and air drying, but some of the 40% MC blocks and all of the 80% MC blocks had to be autoclaved and infiltrated under vacuum to force sufficient water into the wood. The blocks were allowed to equilibrate their moisture contents in sealed polyethylene bags for 6 days at the three higher moisture content levels and for 14 days at the lower moisture content levels before capsules containing MIT were sealed into the blocks with serum caps. The treated blocks were stored in polyethylene bags (water impermeable, but MIT permeable) for 7 days, after which the blocks were split and the capsules removed.

The capsules were air dried in a laboratory fume hood for 1 day to reseal the capsules and prevent further MIT loss, and then they were weighed and weight losses were determined from their original weights. Capsules were reweighed after air drying for a 2 nd day, and one capsule that failed to reseal and continued to leak MIT between the 1 st and 2 nd days of drying was discarded. The block moisture contents during the 7 day incubation period decreased 1-2%, but all blocks within each moisture group were within a 0.5-1.5% range of the average moisture contents.

Capsules incubated in wood at 18-19% MC lost MIT slowly, but as the moisture content of the wood blocks increased, the rate of fumigant release increased rapidly to a near maximum at 28-31% MC (Table 7). This moisture content corresponds closely to the fiber-saturation point of the wood, and suggests that if free water is present in the wood surrounding the gelatin capsules, the capsules will release MIT for movement into the wood. MIT

release from capsules in wood at 35-39% MC continued at the maximum rate and was not significantly different than in the 28-31% MC wood ($t=0.771$, $df=7$, $P>0.4$), but decreased in wood at 75-79% MC, probably due to restricted diffusion of the MIT through the wood and away from the capsules in wood at this high moisture content. This suggests that the addition of a small quantity of water to the treatment holes along with the capsules should be sufficient to release the MIT from the gelatin capsules, but too much water may hinder the release of MIT and its subsequent movement through wood.

Effectiveness of Gelatin Encapsulated Methylisothiocyanate in Blocks Infested With Poria carbonica

Small wood blocks were treated with either gelatin encapsulated MIT or non-encapsulated MIT to compare their relative effectiveness. Douglas-fir heartwood blocks (2.5 cm square by 10 cm grain length) were soaked in sterile distilled water for 30 minutes, and then autoclaved for 30 minutes at 18 psi. This brought the wood to about 30% MC. The sides of the blocks were then coated with paraffin wax, and the ends of the blocks were inoculated by placing a 2.5 cm square of agar cut from an actively growing colony of P. carbonica such that the fungal growth was pressed against the end grain of the block. A 2.5 cm square by 1.0 cm long water-saturated and autoclaved Douglas-fir wafer was secured over the inoculated ends of each block with rubber bands. The blocks were incubated for 6 weeks at 20-23°C in plastic crispers containing sterile distilled water to maintain

Table 7. Influence of wood moisture content on the release of methylisothiocyanate (MIT) from gelatin capsules

Percent wood moisture[1]	Mean MIT loss from 5 capsules during a 1 week incubation period in wood	
	Weight loss mg/capsule[2]	MIT loss percent (± 1 SE[3])
Control[4]	2	0.2 (0.04)
18-19	20	2.0 (0.16)
20-23	90	9.3 (0.38)
23-25	304	31 (2.35)
28-31	753	75 (3.33)
35-39	762	78 (2.59)
75-79	586	60 (1.93)

[1] Moisture content range in the Douglas-fir heartwood blocks includes the initial and final moisture contents for the period the capsules were in the blocks.

[2] Initial capsule weights were about 1200 mg (1000 mg of MIT and 200 mg of gelatin capsule).

[3] Standard error.

[4] Capsules were incubated in a fume hood.

a high humidity.

After incubation, a 6 mm diameter by 22 mm deep hole was drilled at midlength in each block, and the blocks were treated in groups of four with either gelatin encapsulated MIT (#4 capsules), or non-encapsulated MIT, at the following concentrations: 0 mg, 25 mg, 50 mg, 102 mg, and 203 mg per block. Water (300 µl) was added to holes containing MIT capsules and all treatment holes were sealed with serum caps. The blocks were incubated for 7 days before two 5 mm long cross sections were cut from each end of the blocks. The outer 5 mm cross sections were discarded and the inner cross sections were used to determine fungal viability. Four 6 mm square blocks were cut from the center of each cross section, lightly flamed, and then plated on PDA containing 1% agar, 10 ppm benomyl, and adjusted to pH 3.5 with lactic acid. A drop of water containing 10 ppm benomyl was also placed on each plated wood square to help control fungi contaminates. Plates were incubated for at least 4 weeks to determine the viability of P. carbonica in the wood.

Gelatin encapsulated MIT was as effective as non-encapsulated MIT in controlling P. carbonica in this wood block test, and appeared to be even slightly more toxic at the lowest concentration tested even though this difference was not statistically significant (Table 8). This demonstrates that MIT is released from gelatin capsules in the small wood blocks at a rate and concentration that makes it as effective as when the MIT is applied directly to the wood.

Table 8. Effectiveness of methylisothiocyanate (MIT) applied in gelatin capsules to Douglas-fir heartwood blocks infested with P. carbonica

MIT Treatment	Percentage inhibition of P. carbonica in wood at various fumigant concentrations (mg MIT/block)[1]			
	203	102	50	25
Gelatin encapsulated	84	78	37	19
Non-encapsulated	87	75	44	6

[1] Incubation period was 7 days. Each value is based on the recovery of P. carbonica from 32 cubes (four cubes cut from each end of four blocks). Fungus inhibition in gelatin encapsulated treatments were not statistically different than in non-encapsulated treatments ($t < 1.2$, $df=14$, $P > 0.2$ at each MIT concentration).

Methylisothiocyanate Treatments of Douglas-fir Pole Sections

Wood pole sections were used to compare the concentration and movement of MIT vapor through wood treated with gelatin encapsulated MIT, non-encapsulated MIT, and Vapam. In addition, the amount of water required for adequate release of MIT from capsule treatments was determined. Fifteen Douglas-fir pole sections (2.6 meter by 25-33 cm diameter) were end-painted with "lumber seal" to retard end penetration by preservatives and the sections were pressure treated with pentachlorophenol in heavy oil[1]. A single treatment hole (2.1 cm diameter by 24 cm deep) was drilled at a 30^{o} angle downward at 0.75 meter from the butt end of each pole section. Three vapor sampling holes (1.1 cm diameter by 16.5 cm deep) were drilled perpendicular to the surface of each pole at 0.3, 0.6, and 1.2 meters directly above the treatment holes. The two more distant vapor sampling holes were slightly offset to opposite sides of the first sampling hole to minimize interference of the closer sampling holes on the diffusion of MIT to the more distant sampling holes. The sampling holes were sealed with rubber serum caps glued in place with a silicone sealent. All holes were positioned to avoid major checks, and spiral grain was taken into account during vertical alignment of the sampling holes.

Pole sections were treated with one of five different fumigant treat-

[1] Pole sections were treated and donated by McCormick & Baxter Creosoting Company.

ments: 80-88 ml of Vapam, 45 ml of non-encapsulated molten MIT, or 45 ml of gelatin encapsulated MIT with either 40, 25, or 15 ml of water added to each treatment hole along with the capsules to aid fumigant release. The 80-88 ml of Vapam used was the amount required to completely fill each treatment hole. The maximum amount of encapsulated MIT that could easily be placed in similar treatment holes was 45 ml, distributed between two 1.9 cm diameter by 9.5 cm long gelatin capsules, and the greatest quantity of water that could be added along with the capsules to each treatment hole was 40 ml. Non-encapsulated MIT at 45 ml per treatment hole was used to enable direct comparison with encapsulated treatments. All treatment holes were sealed with 5 to 6 cm long papaffin wax coated heartwood plugs 2.2 cm in diameter.

Poles were treated on 26 August 1982 and were then stored vertically in two rows outside in Corvallis, OR. One Vapam treated pole section leaked Vapam through a check during treatment and was therefore discarded from this study. MIT vapor concentrations in the pole sections were monitered periodically for over 52 weeks by removing 4.5 ml vapor samples from the sampling holes and analysing the samples for MIT content by GLC. The air temperature during sampling varied from 1-24^{o}C. Vapor concentrations of MIT were adjusted to the concentrations expected at 20^{o}C based on the average air temperature during sampling and the corresponding MIT vapor pressures as listed by Bauer and Burskkies (1935). This did not completely eliminate fluctuations in MIT concentrations between sampling dates,

probably because the temperature within the wood was different from that measured outside.

Fumigant vapors were first detected in sampling holes 0.3 meter above the treatment holes after 1-2 weeks in the MIT treated pole sections, but MIT vapors in Vapam treated pole sections were not detected at this level until almost 5 weeks after treatment (Fig. 5). Movement of MIT vapors to sampling holes 0.6 meter above treatment holes was much slower, requiring between 14 and 30 weeks before fumigant vapors were detected in the MIT treated pole sections (Fig. 6), and fumigant vapors were never detected even after 52 weeks in Vapam treated poles. MIT vapors were not detected at 1.2 meter above the treatment holes until 49 weeks, and then in only two of the 12 MIT treated poles. This rate of vertical movement of MIT vapors through these pole sections was slower than the 0.3-0.6 meter per month previously reported for Vapam and chloropicrin (Scheffer and Graham, 1975). Scheffer and Graham used a bioassay to study the rate of fumigant movement through untreated Douglas-fir poles (about 37% MC) that were stored inside. The fumigant movement may have been slower in our treated pole sections because they were stored outside and exposed to the cooler winter temperatures, and the pole sections were drier (about 20 to 25% MC at 6.5 cm), possibly allowing the wood to tie up more fumigant. In addition, our GLC determination of vapor concentrations of MIT may have been less sensitive than the bioassay used by Scheffer and Graham, and, since their bioassay was not specific to MIT, it may have responded to

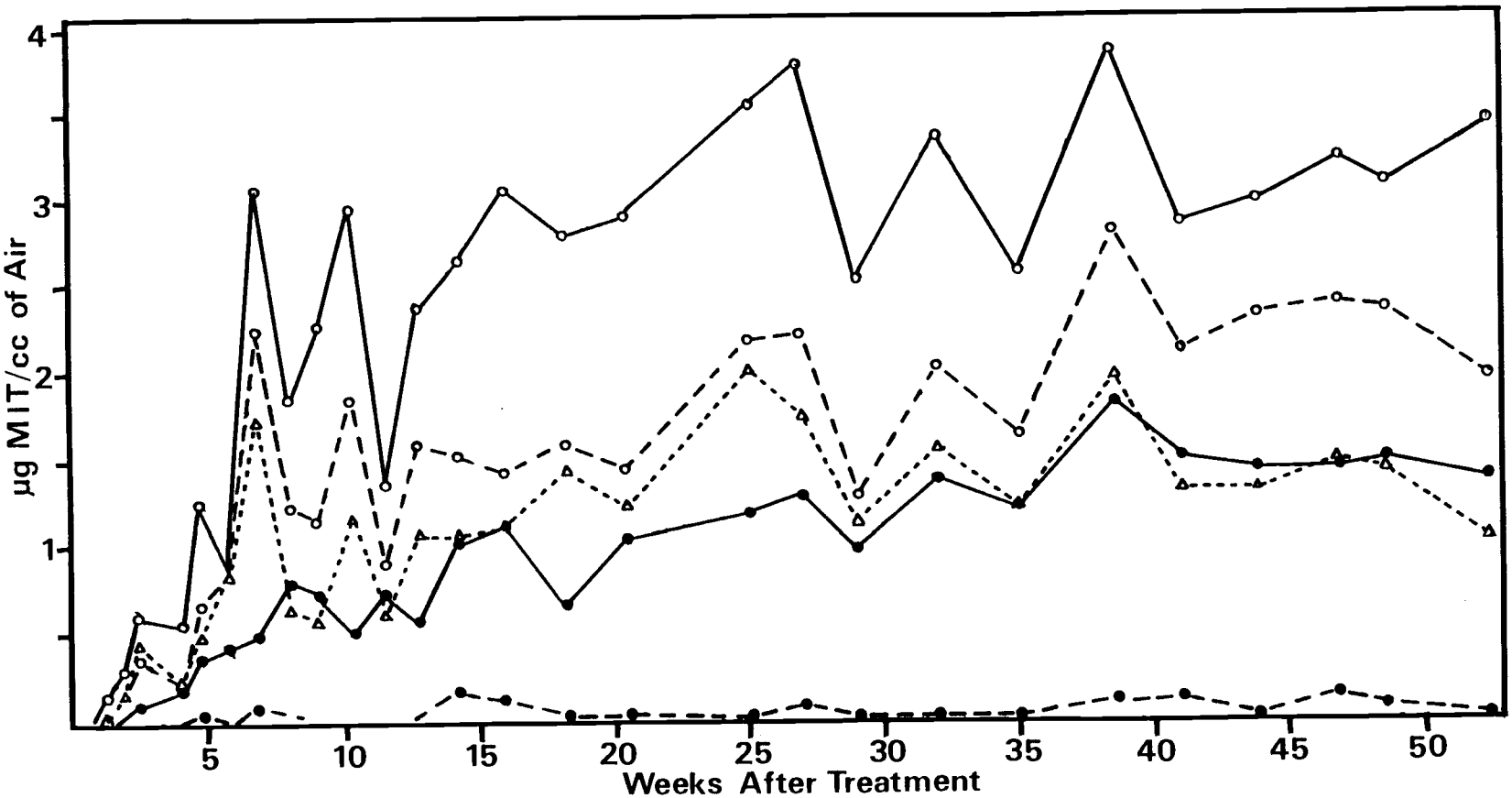

Fig. 5. Average methylisothiocyanate (MIT) vapor concentrations over time monitered in Douglas-fir pole sections 0.3 meter above the treatment sites. Treatments involved either 80-88 ml of Vapam •——•, 45 ml of non-encapsulated MIT •——•, and 45 ml of gelatin encapsulated MIT with either 15 ml of water o——o, 25 ml of water o– –o, or 40 ml of water Δ----Δ. Water was added to the treatment holes along with the capsules to aid fumigant release. MIT vapor concentrations were adjusted to the expected concentrations at 20°C based on the air temperature during sampling and the corresponding MIT vapor pressures.

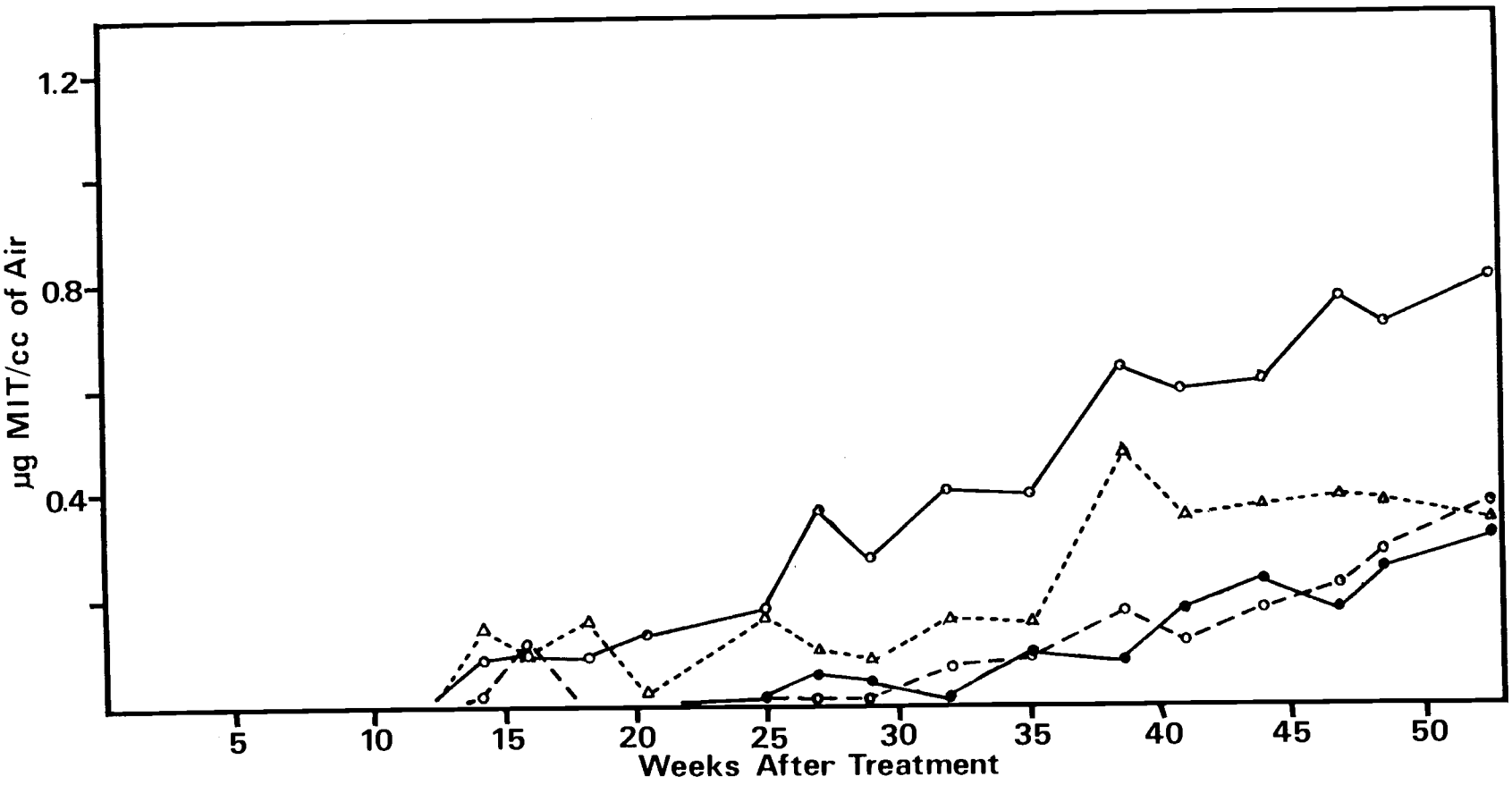

Fig. 6. Average methylisothiocyanate (MIT) vapor concentrations over time monitered in Douglas-fir pole sections 0.6 meter above the treatment sites. Treatments involved either 45 ml of non-encapsulated MIT ●——●, and 45 ml of gelatin encapsulated MIT with either 15 ml of water o——o, 25 ml of water o- - -o, or 40 ml of water Δ- - -Δ. Water was added to the treatment holes along with the capsules to aid fumigant release. MIT vapor concentrations were adjusted to the expected concentrations at 20°C based on the air temperature during sampling and the corresponding MIT vapor pressures.

other unknown variables.

Vapam treated poles never had high MIT vapor concentrations at 0.3 meter above the treatment holes during the monitering period. These concentrations were often at the lower limit of GLC resolution and, at times, could not be quantified.

Although the amount of Vapam added to each pole section should have theoretically yielded the same amount of MIT as 19 ml of the active material, the recovery of MIT vapor at 0.3 meter above the Vapam treatment holes was often less than about 1/15 of that recovered from pole sections treated with 45 ml of MIT (Fig. 5). One explanation for the low MIT recovery from Vapam treated poles is that the conversion of sodium N-methyl dithiocarbamate to MIT in Douglas-fir heartwood occurred with less than 100% effeciency.

To test this, 0.2 g of Douglas-fir heartwood sawdust (8.5% MC) was moistened with 0.3 ml of water and placed in each of four 250 ml glass stoppered Erlenmeyer flasks. Small glass vials containing 7.5 ml of chromatographic grade ethyl acetate were sealed with parafilm and added to each flask. The flasks were then treated by pipetting either 400 µl of Vapam, or 86 µl of pruified MIT (the amount of MIT expected from 400 µl Vapam) onto the sawdust in the flasks, and sealing the glass stoppers in place with a silicone stopcock grease. After 20 hr, the ethyl acetate was spilled from the vials and allowed to extract the contents of the flasks for 3 hr, after which the MIT content was determined by GLC. The MIT concentrations recover-

ed from Vapam treated chambers were only 34-38% of the concentration detected in MIT treated chambers. This experiment was repeated using unmoistened sawdust and a 10 hr incubation period, with a 39-42% recovery of MIT from the Vapam. Although it has been shown that Douglas-fir sawdust facilitates the rapid decomposition of Vapam to volatile toxicants (Graham and Corden, 1980), it appears that the production of MIT by Vapam when applied to wood is only about 40%.

Turner and Corden (1963) reported that 70-87% of the Vapam applied to soil was accounted for as MIT, depending of the treatment conditions. Since soil pH influences Vapam conversion to MIT, with decreasing conversion as acidity increases (Turner and Corden, 1963: and Goring, 1972), the poor conversion of Vapam to MIT observed in wood may be due to the acidic pH of wood. Vapam may break down to other fungitoxic materials in wood besides MIT, but these materials were not detected with our GLC methods.

The highest average MIT vapor concentrations 0.3 and 0.6 meter above treatment holes were observed in pole sections treated with gelatin encapsulated MIT and the lowest quantity of water, i.e. 15 ml (Fig. 5 and Fig. 6). The gelatin encapsulated treatments as a group also appeared to produce higher MIT vapor concentrations moving through the pole sections than the non-encapsulated treatments. These differences, which are illustrated graphically in Figs. 5 and 6, are based on average concentrations measured in groups of three replicate poles. The MIT concentrations at any given time period often varied between replicates, especially shortly

after treatment, when fumigant vapors were often detected at sampling sites more rapidly in some replicate pole sections than in others.

To determine if there were any statistically significant differences between the four MIT treatments, comparisons were made between cumulative MIT concentrations X times (total fumigant doses) moving through the individual pole sections 0.3 meter above the treatment sites (Table 9). After 42 weeks, the total MIT dose moving through the pole sections was significantly greater in the treatments using encapsulated MIT with 15 ml of water added than in the other three MIT treatments. Although the mean dose of fumigant was always much higher in the encapsulated treatments with 15 ml of water added, during the time periods less than 42 weeks after treatment, the significance of this difference with the other three treatments was lost. A significant difference in fumigant doses moving through the pole sections was never observed between the non-encapsulated MIT and the encapsulated MIT with 40 or 25 ml of water added with the treatments.

It was unexpected that the encapsulated MIT treatments with 15 ml of water added would produce significantly higher MIT vapor concentrations moving through the pole sections than the other three MIT treatments. The addition of only 15 ml of water along with encapsulated treatments was sufficient for excellent fumigant release and movement into the wood, whereas the larger quantities of water (25 and 40 ml) apparently hindered the movement of fumigant vapor through the wood. This experiment was initiated just prior to the wet winter months (Oct-April) and it is not yet known

Table 9. Statistical comparison of encapsulated and non-encapsulated methylisothiocyanate (MIT) treatments of Douglas-fir pole sections using the Student-Newman-Keuls test (α =0.05, df=8)

Time period (weeks)	Non-encapsulated MIT $\bar{Y}_1$ [1]	Encapsulated MIT and 40 ml water $\bar{Y}_2$	25 ml water $\bar{Y}_3$	15 ml water $\bar{Y}_4$
0- 9.1	3.22	5.31	6.49	10.64
0-18.3	10.59	14.78	20.28	23.12
0-29	22.04	31.62	39.90	68.50
0-41.1	39.27	50.04	64.99	106.43
0-52.9	56.48	65.01	91.66	143.47
20.4-52.9	44.07	47.42	68.10	103.34

[1] $\bar{Y}$ values are based on cumulative MIT concentrations X times (weeks · µg MIT/ml air) moving through the individual pole sections 0.3 meter above treatment sites during the specified time periods. Groups of underlined means are not statistically different.

whether the smaller quantity of water used would have been sufficient for optimum MIT release when applied during the warmer and drier summer months. The addition of 15 ml of water with the encapsulated treatments produced significantly higher doses of fumigant vapors moving 0.3 meter above treatment holes than in non-encapsulated treatments. It is possible that the addition of this water benefited the movement of fumigant upward through the wood by filling the tracheids below the treatment holes and thus slowing fumigant movement downward through the pole sections, whereas the larger quantities of water may have been sufficient to retard movement in both directions. Also, it was shown earlier that wet wood sorbed a lower quantity of fumigant than dry wood (Fig. 4), suggesting that the addition of a small quantity of water along with encapsulated treatments might reduce the amount of MIT bound to the wood and result in more fumigant being available to move through the poles.

While Vapam is effective in controlling decay fungi in utility poles, it has shown poor residual effectiveness compared to Vorlex (20% MIT), with a virtual absence of fungitoxic vapors in wood 10 years after treatment (Graham and Corden, 1980). Treatment of pole sections with encapsulated MIT produced much higher fumigant concentrations moving through poles than Vapam treatments in similar sized treatment holes, probably because of the poor conversion of Vapam to MIT in wood. This effect is an important consideration in the treatment of wood products serving a structural function; where size and number of treatment holes that can safely be

drilled into the product is limited, and the maximum amount of active ingredient to achieve greatest control and residual effectiveness is desired.

Gelatin satisfies the requirements for an ideal MIT encapsulating material as it is inert to MIT, impermeable to fumigant loss under dry storage conditions, and will rapidly release MIT when placed in wood and moistened. Gelatin encapsulated MIT treatments were equally as effective as non-encapsulated treatments in controlling decay fungi in small wood block tests, and required the addition of only a small quantity of water per treatment hole in pole sections to release and allow excellent fumigant movement through the wood.

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